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Synthesis, Characterization, and Molecular Structure of Halogen Oxidation Products of Ruthenocene

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Oxidation of ruthenocene by iodine and bromine gives $[Ru(cp)_2I]I_3$ and $[Ru(cp)_2Br]Br_3$, respectively. The crystal structure of the triiodide salt of $Ru(cp)_2I^+$ has been determined from 1093 independent counter-diffractometer intensities. The compound crystallizes in the orthorhombic space group *Pnma* with unit cell of dimensions $a = 7.632$, $b = 14.080$, and $c = 14.186$ Å. Assuming four molecules per unit cell, the calculated and observed densities are 3.22 and 3.14 g cm^{-3}, respectively. Least-squares refinement of all nonhydrogen atoms resulted in a conventional *R* factor of 8.9%. The cation $Ru(cp)_2I^+$ has crystallographically imposed C_s symmetry. The cyclopentadienyl rings in $Ru(cp)_2I^+$ are eclipsed; each ring is tilted back by 16° to accommodate the iodide ligand. The structural assignment for $[Ru(cp)_2Br]Br_3$ is based on a comparison of its infrared spectrum to that of the iodo derivative and the presence of an electronic absorption band attributable to Br_3^-.

Introduction

Attempts to prepare and study the ruthenicenium ion, $Ru(cp)_2^+$, which was first reported in 1952 by Wilkinson,[1] have resulted in the characterization of several interesting ruthenocene derivatives. Electrochemical oxidation of $Ru(cp)_2$ at a mercury anode by Wilkinson's method[1] yields[2] a diamagnetic Hg-bridged complex, $[(cp)_2Ru-Hg-Ru(cp)_2]^{2+}$, whereas chemical oxidation by halogens produces diamagnetic haloruthenocene(IV) complexes. Although we have explored a wide variety of oxidative conditions we have not been able to prepare the simple one-electron oxidation product, $Ru(cp)_2^+$. In this paper we report synthetic details and the results of structural studies of the haloruthenocene(IV) complexes.

Experimental Section

Compound Preparation. Ruthenocene (Orgmet) was purified by recrystallization in ethanol and sublimation twice under vacuum. All other chemicals used were reagent grade unless specified. Chemical analyses were performed by Schwarzkopf Microanalytical Laboratory.

Chemical oxidation of ruthenocene was carried out using halogens as oxidizing agents. A sample of ruthenocene (0.5 mmol) dissolved in 50 ml of CCl_4 was added to a 500-ml CCl_4 solution containing 1.5 mmol of iodine. A dark red crystalline precipitate (compound I) slowly formed. This iodide compound was found to be diamagnetic. Several attempts using different ratios of the reactants $Ru(cp)_2$ and I_2 and different solvents such as cyclohexane, *n*-hexane, and benzene failed to produce any paramagnetic oxidation products. Bromine oxidation of ruthenocene proceeded in a similar fashion. To 150 ml of a cyclohexane solution of ruthenocene (0.10 g), bromine was added dropwise until the reaction was complete. A greenish yellow precipitate (compound II) was formed. This compound was also found to be diamagnetic.

Both of the halide complexes (I and II) are soluble in polar organic solvents. The bromide complex (II) is unstable as a solid, decomposing after a few days at room temperature, and dissolves with reaction in water. On the other hand, the iodide (I) is so stable that it can be purified by recrystallization in nitromethane; well-formed needles were grown from this solvent. Analytical data for compounds I and II are consistent with the following formulas. *Anal.* Calcd for I, $Ru(C_5H_5)_2I_4$: Ru, 13.68; I, 68.70; C, 16.26; H, 1.36. Found: Ru, 13.39; I, 68.04; C, 16.07; H, 1.50. Calcd for II, $Ru(C_5H_5)_2Br_4$: Ru, 18.34; Br, 58.02; C, 21.80; H, 1.83. Found: Ru, 18.02; Br, 57.44; C, 21.97; H, 1.89.

Physical Measurements. The electronic absorption spectrum of compound II was measured on a Cary Model 14 CMRI spectrophotometer. A Cary Model 14 was employed for spectral measurements near 2000 Å. Acetonitrile was used as the solvent in these absorption measurements. Infrared spectra of the two compounds were obtained with a Perkin-Elmer Model 225 grating spectrophotometer. Nujol mulls were used for the 200–450-cm^{-1} region and both KBr pellets and Nujol mulls for the 450–4000-cm^{-1} region. Room-temperature magnetic susceptibilities of solid materials were determined with a Princeton Applied Research FM-1 vibrating sample magnetometer.

X-Ray Measurements and Calculational Details. Preliminary precession photography showed compound I to belong to the orthorhombic system. The systematic absences *hk*0, $h = 2n + 1$, and 0*kl*, $k + 1 = 2n + 1$, imply the space group is either *Pnma* or $Pn2_1a$. Successful solution of the structure showed the centrosymmetric *Pnma* to be correct. The unit cell parameters were determined by least-squares refinement[3] of nine reflections carefully centered on a diffractometer (Zr-filtered Mo Kα radiation). The cell constants obtained are $a = 7.632$ (7), $b = 14.080$ (10), and $c = 14.186$ (7) Å. Assuming four formula weights in the unit cell, the calculated density of 3.22 g cm^{-3} is in satisfactory agreement with the observed 3.14 g cm^{-3} determined by flotation.

Three-dimensional intensity data were collected from a rod-shaped crystal measuring approximately 0.1 × 0.1 × 0.2 mm, using a Datex-automated General Electric XRD-6 diffractometer with Zr-filtered Mo Kα radiation. Intensity measurements were made using a θ–2θ scan at a rate of 2°/min over a 2.5° range to a 2θ maximum of 55°. The peaks were centered in the scan, and 30-sec background counts were taken at the beginning and end of each scan. Three standard reflections were checked during the 89-hr collection period and the intensities of these reflections showed a linear decrease of 21 ± 2% over this time period. All intensities were corrected for this decomposition. Lorentz and polarization corrections were also applied to the data. Squared standard deviations in the intensities were computed from counting statistics with an additional term of $(0.2S)^2$, where *S* is the scan count, added to compensate for nonstatistical errors. All measured structure factors less than three standard deviations were excluded from the least-squares refinement. Standard heavy-atom techniques were employed to locate the ruthenium and iodine atoms from the three-dimensional Patterson map. The carbon atoms were found by Fourier synthesis. Using scattering factors[4] corrected for real dispersion effects[5] for iodine and ruthenium, the structure was refined by full-matrix least-squares methods.

The quantity minimized was $\Sigma w(F_o^2(1/K^2)F_c^2)^2$, where individual weights were assigned, $w = 1/\sigma^2(F_o^2)$. With the heavy atoms anisotropic and the carbon atoms isotropic, the refinement proceeded to a conventional *R* factor ($R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$) of 8.9%. Efforts to refine the carbon atoms anisotropically resulted in C_4 always becoming nonpositive definite and in only slight improvement in the *R*-factor to 8.4%.

An effort to refine the structure in the space group $Pn2_1a$ also resulted in only a slight decrease in the *R* factor, indicating the centrosymmetric choice to be correct. The lack of an absorption

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[3] All calculations were performed on an IBM 360 computer using the Caltech CRYM system of crystallography programs: D. J. Duchamp, Paper B-14, American Crystallographic Association Meeting, Bozeman Mont., 1964. The ORTEP program of C. K. Johnson was used to produce the figures.

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[5] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table I. Final Parameters and Their Standard Deviations (in Parentheses) from Least-Squares Refinement

Atom	x/a	y/b	z/c	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I1	0.14846 (40)	0.25^b	0.15015 (22)	0.02937 (61)	0.00524 (15)	0.00891 (18)	0.0^b	0.01636 (55)	0.0^b
I2	0.50971 (28)	0.25^b	−0.32647 (14)	0.01492 (39)	0.00618 (13)	0.00327 (8)	0.0^b	−0.00115 (39)	0.0^b
I3	0.49684 (19)	0.45758 (11)	−0.33177 (10)	0.01965 (32)	0.00521 (9)	0.00572 (8)	−0.00036 (30)	−0.00101 (34)	−0.00285 (14)
Ru	0.45199 (34)	0.25^b	0.04803 (17)	0.01603 (47)	0.00184 (11)	0.00329 (11)	0.0^b	0.00048 (40)	0.0^b

Atom	x/a	y/b	z/c	B, Å^2
C1	0.3533 (30)	0.3939 (16)	0.01974 (15)	5.08 (0.51)
C2	0.4467 (27)	0.3958 (15)	0.1043 (14)	4.36 (0.45)
C3	0.6183 (31)	0.3714 (18)	0.0882 (17)	5.90 (0.58)
C4	0.6319 (34)	0.3526 (18)	−0.0120 (18)	6.13 (0.58)
C5	0.4616 (28)	0.3677 (17)	−0.0551 (16)	5.44 (0.50)

[a] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] No deviation; these parameters are fixed by symmetry.

Table II. Interatomic Distances (Å) and Angles (deg) for $[Ru(cp)_2I]I_3$

Distances

I2–I3	2.925 (3)	C2–C2′	4.11 (3)
Ru–I1	2.732 (4)	C3–C3′	3.42 (4)
Ru–C1	2.20 (2)	C4–C4′	2.89 (4)
Ru–C2	2.20 (2)	C5–C5′	3.32 (3)
Ru–C3	2.21 (2)	I1–C1	3.16 (2)
Ru–C4	2.17 (2)	I1–C2	3.13 (2)
Ru–C5	2.21 (2)	I1–C3	4.07 (2)
C1–C2	1.40 (2)	I1–C4	4.58 (3)
C2–C3	1.37 (3)	I2–C5	4.11 (2)
C3–C4	1.45 (4)	Av Ru–C	2.197 ± 0.012
C4–C5	1.45 (4)	Av C–C	1.41 ± 0.03
C5–C1	1.34 (3)	Ru–ring	1.84
C1–C1′	4.05 (3)		

Angles

I3–I2–I3′	175.2 (0.2)	I–Ru–C1	78.8 (1.0)
C1–C2–C3	110 (2.0)	I–Ru–C2	78.0 (1.0)
C2–C3–C4	106 (2.0)	I–Ru–C3	110.5 (1.0)
C3–C4–C5	109 (2.0)	I–Ru–C4	138.2 (1.0)
C4–C5–C1	104 (2.0)	I–Ru–C5	112.3 (1.0)
C5–C1–C2	111 (2.0)	Av C–C–C	108.0 ± 2.2

Table III. Electronic Absorption Spectrum of $[Ru(cp)_2Br]Br_3{}^a$

$\bar{\nu}$, cm^{-1}	ϵ	f
$25{,}600^b$	1,800	
37,200	34,000	~0.70
$46{,}500^b$	31,000	
48,800	34,000	

[a] Acetonitrile solution at 300°K. [b] Shoulder.

correction and the crystal decomposition apparently resulted in data which do not yield an improved fit. The final goodness of fit, $[\Sigma w(F_o^2 - F_c^2/K^2)^2/n - p]^{1/2}$, is 1.06. A final difference Fourier with isotropic carbon atoms revealed a peak with a height corresponding to 2 e/Å^3 between carbon atoms C4 and C5. No other peak exceeded two electrons in the region of the ring and there was no indication of ring disorder. The final positional and thermal parameters are given in Table I. The observed and calculated structure factors are available.[6]

Results and Discussion

Molecular Structure. Analytical data for compounds I and II are in excellent agreement with the empirical formulation $Ru(cp)_2X_4$ (X = I, Br). Both compounds are diamagnetic. The X-ray determination on the iodine oxidation product establishes its molecular structure to be $[Ru(cp)_2I]I_3$. That $Ru(cp)_2I^+$ results from iodine oxidation of ruthenocene is not particularly surprising in light of the observation[7] that oxidation of osmocene by iodine in aqueous sulfuric acid results in the species $Os(cp)_2I^+$. Furthermore, a chronopotentiometric study[8] of various metallocenes has shown that the oxidation of ruthenocene is a one-step, two-electron process.

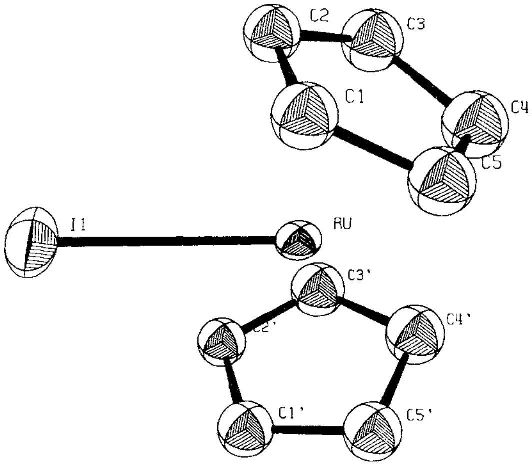

Figure 1. Structure of the cation $Ru(cp)_2I^+$. Thermal ellipsoids drawn for 30% probability.

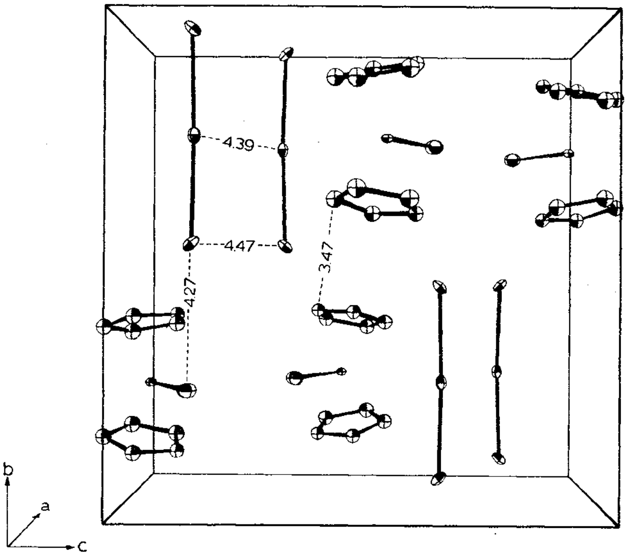

Figure 2. View of the *xz* plane. Shortest intermolecular distances shown. Thermal ellipsoids drawn for 30% probability.

A view of the structure of $Ru(cp)_2I^+$ is shown in Figure 1. Intramolecular bond lengths and angles for both the cation and the triiodide ion are given in Table II. It is interesting to compare the molecular structure parameters of the cation

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[6] See paragraph at end of paper regarding supplementary material.

[7] E. O. Fischer and H. Grubert, *Chem. Ber.*, **92**, 2302 (1959).

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Table IV. Infrared Spectral Data for $Ru(cp)_2$ and $[Ru(cp)_2X]X_3$[a]

$Ru(cp)_2$	$[Ru(cp)_2I]I_3$	$[Ru(cp)_2Br]Br_3$	$Ru(cp)_2$	$[Ru(cp)_2I]I_3$	$[Ru(cp)_2Br]Br_3$
	211 m	225 w	1002 s[b]	1020 m	1013 m
379 w	379 m	377 m	1050 w[b]	1045 w[b]	1050 w[b]
446 s	419 m	429 m	1100 s[b]	1107 w	1112 w
	578 w	579 w	1402 s	1402 s	1404 s
806 s	819 w	818 w		1436 m[c]	1440 s[c]
834 w	844 s	840 s	1620 w		
864 m		864 w	1660 w		
	920 w	920 w	1675 w		
	976 w	975 w	1755 w		
			1790 w		
			3080 m[b]	3090 s	3085[b]

[a] Positions of bands were taken from Nujol mull spectra. [b] Band shows further structure in a KBr pellet. [c] Band position taken from KBr pellet spectrum.

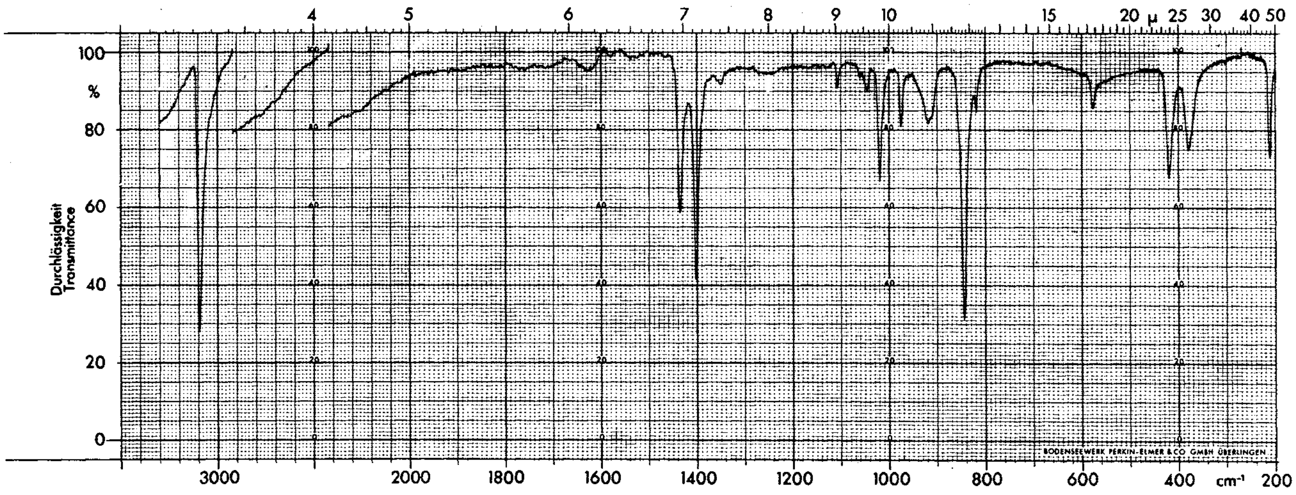

Figure 3. Infrared spectrum of $[Ru(cp)_2I]I_3$: KBr pellet in the 4000–450-cm^{-1} region; Nujol mull in the 450–200-cm^{-1} region.

with those previously obtained for ruthenocene[9] and ferrocene.[10] The average ring C-C bond length in $Ru(cp)_2I^+$, 1.41 ± 0.03 Å, is comparable to those obtained for ruthenocene (1.43 ± 0.03 Å) and ferrocene (1.40 ± 0.02 Å). The average metal-carbon distance in $Ru(cp)_2I^+$ is 2.20 ± 0.01 Å, whereas in ruthenocene this distance is 2.21 ± 0.02 Å. In going from $Ru(cp)_2$ to $Ru(cp)_2I^+$ the metal is formally oxidized from Ru(II) to Ru(IV). With an increase in metal oxidation state we might expect a decrease in metal-carbon distance, but steric interactions between the ring carbons and iodine apparently prevent appreciable shortening. Further evidence for steric strain in the cation can be deduced from the length of the ruthenium-iodine bond. The observed distance of 2.732 (3) Å is slightly longer than the 2.719 (7) Å distance found in $Ru(CO)_4I_2$[11] in spite of the much larger formal charge on ruthenium in $Ru(cp)_2I^+$.

It is clear from Figure 1 that the cyclopentadienyl rings are tilted back to allow coordination of iodine to the ruthenium. A least-squares plane $0.2279x - 0.9608y - 0.1582z + 5.899 = 0$ was calculated for the cyclopentadienyl ring. The average deviation of the carbon atoms from the least-squares plane was found to be very small (0.002 Å), with the greatest deviation being 0.003 Å. The angle between the ring planes was calculated to be 32.2°. The rings remain eclipsed as they are in ruthenocene, however, in spite of their nonplanarity.

The triiodide ion, I_3^-, in this structure is required to be symmetrical by the mirror plane. The iodine-iodine bond distance is found to be 2.925 ± 0.003 Å, in agreement with previously reported values [*e.g.*, 2.928 ± 0.0025 Å for one modification of $(C_2H_5)_4NI_3$].[12] In some crystals the I_3^- ions have been observed to deviate from linearity.[13] Such is the case here, where ∠I-I-I was found to be 175.14 ± 0.1°. Reference to the packing diagram (Figure 2) provides some insight into the cause of this nonlinearity. The two triiodide ions are at near van der Waals contact. It can be seen that the more negative terminal iodide atoms have repelled each other to a greater extent than the central iodines.

The electronic absorption spectrum of $Ru(cp)_2Br_4$ was measured in acetonitrile solution at room temperature; the results are given in Table III. The most interesting feature in this spectrum is the intense (ϵ 34,000) band at 37,200 cm^{-1}. We assign this band to Br_3^-, as this ion has an absorption peak[14] at 36,800 cm^{-1} in acetonitrile solution with an intensity comparable to that observed in the present case. This observation taken together with striking infrared spectral similarities to $[Ru(cp)_2I]I_3$ (*vide infra*) make it probable that the molecular structure of the product of bromine oxidation of ruthenocene is $[Ru(cp)_2Br]Br_3$.

Infrared Spectra. The infrared spectra of the $Ru(cp)_2X^+$ complexes (Table IV and Figure 3) show that the fundamental modes of the ring-localized motions are in essentially the same positions as in ruthenocene. The low-energy band (211 cm^{-1}) of $[Ru(cp)_2I]I_3$ represents a skeletal motion not ob-

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(9) G. L. Hardgrove and D. H. Templeton, *Acta Crystallogr.*, **12**, 28 (1959).

(10) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956).

(11) L. F. Dahl and D. L. Wampler, *Acta Crystallogr.*, **15**, 946 (1962).

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served for ruthenocene; it is assignable to either Ru-X stretching or ring-metal-ring bending. The ring-metal-ring bending motion, ω_{22}, of ruthenocene was calculated[15] to be ~185 cm^{-1} by using the ω_4/ω_{22} ratio of ferrocene. Here ω_4 is the symmetrical ring-metal-ring stretch. A low-energy band appears at 225 cm^{-1} in [Ru(cp)$_2$Br]Br$_3$. If this band is the ring-metal-ring bending vibration in ruthenocene shifted to higher energy by ring crowding caused by the halogen substitution, it would be reasonable to expect the iodo-substituted molecule to exhibit the higher energy vibration. Thus the observed shift in this low-energy band in going from the iodo to the bromo complex is in better agreement with the Ru-X stretching mode assignment. It may be pointed out that the antisymmetrical ring-metal-ring stretching frequency at 446 cm^{-1} in ruthenocene is lowered to 419 cm^{-1} in [Ru(cp)$_2$I]I$_3$, which indicates that the bonding between the metal and the rings is weakened. This is further support for assigning the 211-cm^{-1} band of [Ru(cp)$_2$I]$_3$ as the Ru-I stretch instead of the ring-metal-ring bending vibration. The higher energy bands at 578, 920, 976, and 1436 cm^{-1} observed for Ru(cp)$_2$I$^+$ (579, 920, 975, and 1440 cm^{-1} for Ru(cp)$_2$Br$^+$) are all assignable to ring vibrations which do not give rise to observable bands in the more symmetrical ruthenocene molecule.

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Registry No. [Ru(cp)$_2$I]I$_3$, 39427-31-1; [Ru(cp)$_2$Br]Br$_3$, 39427-30-0.

Supplementary Material Available. Calculated and observed structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-301.

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Vibrational and Raman Intensity Analysis of a Ferredoxin Model: $S_2Fe_2(CO)_6$[1]

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Raman and infrared spectra are reported for $S_2Fe_2(CO)_6$, and for the syn and anti isomers of $(CH_3S)_2Fe_2(CO)_6$. The S_2Fe_2 cluster in the former compound is similar to proposed structures for iron-sulfur proteins of the 2Fe-2S* class. Symmetric stretching modes are identified for $S_2Fe_2(CO)_6$, and their frequencies are satisfactorily calculated by a simple force field, all of whose elements have reasonable values. In particular the Fe-Fe stretching force constant, 1.3 ± 0.2 mdyn/Å appears satisfactory for a Fe-Fe single bond. The Raman intensities can be accounted for with a reasonable set of internal coordinate polarizability derivatives. The modes primarily associated with vibrations of the S_2Fe_2 cluster display preresonance Raman enhancement, which is probably associated with cluster electronic transitions in the visible and near-ultraviolet regions.

Introduction

The successful acquisition of Raman spectra for rubredoxin[2] and adrenodoxin[3] suggests that Raman spectroscopy will be useful in exploring structural features of iron-sulfur proteins.[4] Studies in this area are under way in this laboratory, and we report here a vibrational and Raman intensity analysis for a model compound $S_2Fe_2(CO)_6$ whose structure[5] is shown in Figure 1. Supporting data are provided by the analogous compound $(CH_3S)_2Fe_2(CO)_6$,[6] which lacks a sulfur-sulfur bond. The analysis is also of interest in connection with Raman studies of compounds containing metal-metal bonds.[7]

Experimental Section

$S_2Fe_2(CO)_6$ was prepared by the method of Hieber and Beck.[8] Reddish crystals were obtained from the crude product by sublimation at 40° under vacuum. $(CH_3S)_2Fe_2(CO)_6$ (Pressure Chemical Co.) was separated into its syn and anti isomers by King's chromatographic procedure.[9] Spectral quality methylcyclohexane and carbon tetrachloride were deaerated for use as solvents for solution spectra.

Raman spectra were obtained on solutions and crystalline powders sealed in X-ray capillary tubes, using transverse excitation by 6471- and 6764-Å lines of an Ar$^+$-Kr$^+$ mixed-gas laser (Coherent Radiation Model 52 MG). The Raman spectrometer and its calibration have been previously described.[10] Depolarization ratios, ρ_l, were obtained by analyzing the scattered light with a polaroid disk. Raman intensities were measured using 6764-Å excitation. Band areas were determined with reference to the 847-cm^{-1} band of the methylcyclohexane solvent, which was in turn calibrated against the 459-cm^{-1} (ν_1) band of CCl$_4$ in a mixture of the two liquids. Over-

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